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Proceedings of the Combustion Institute 31 (2007) 3369–3376

Proceedings
of the
Combustion
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Selected profiles of high-pressure methanol–air flames in supercritical water

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Abstract

A semi-batch bench-scale visual flame cell system was designed to spontaneously ignite high-pressure flames in supercritical water as a step in evaluating the effect of presence of these flames on supercritical water oxidation of organics. Methanol proportions between 15 and 40 (v/v%) were used as fuel. Oxidation and flame ignition were achieved by injecting a preheated high-pressure air stream into the supercritical water–methanol mixture. Air was preferred to pure oxygen to maintain the practicality and possible full-scale feasibility of the supercritical water flame system. Flames were ignited successfully at methanol fractions between 21 and 35 (v/v%). Ignition zone temperatures up to 1010 °C were measured. High carbon monoxide production rates were observed in both flame and flameless oxidation in the reaction cell. Noticeable concentrations of nitrogen oxides were also present even in the absence of flames. Highest oxidation levels and strongest flame luminosities were observed at 23 (v/v%) methanol. The optimal methanol range for NO_x minimization was found to be 25–30 (v/v%). A near-infrared thermal imaging system was used to obtain accurate visual and thermal gradient images of flame behavior in supercritical water and to propose a mixing-limited ignition scenario in the visual flame cell.

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Keywords: Supercritical water oxidation; Hydrothermal flames; Air–methanol flames; High-pressure flame ignition; Nitrogen oxides (NO_x)

1. Introduction

Water beyond its critical point (374 °C, 21 MPa) acquires non-polar solvent properties and features an enhanced capacity for hydrocarbon and oxygen dissolution in a single homogeneous phase. Numerous investigations have been

carried out into oxidation processes in supercritical water (SCW) [e.g., 1,2]. Flameless supercritical water oxidation (SCWO) has already been established as an efficient medium for destruction of waste streams with up to 20% organic loading, but is less effective when used to oxidize more complex organics and polymers [3]. The presence of a flame in an SCWO system would be expected to enhance the destructive abilities of the SCW medium. However, only a handful of research groups worldwide have carried out practical investigations on flame oxidation regimes in SCW [4–7].

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In our work, a batch experimental system, the visual flame cell (VFC), is designed to spontaneously generate SCW flames using different methanol proportions as fuel, and a preheated air stream as an oxidizing agent. A sapphire window is installed to provide visual access to the interior of the VFC with the objective of describing and analyzing SCW flames. A primary objective of the experimental system is a simple reproducible design where exotic materials and unconventional system components were avoided as much as possible. Hence, air is selected to avoid complications and safety issues associated with high-pressure and temperature handling of pure oxygen, and to simulate a possible full-scale application. The system is also designed for collection and online analysis of gas and liquid products of SCWO by flames generated in the batch VFC system.

Our investigation is based on the premise that before the destructive ability of the flame processes in SCW could be studied, an evaluation of the environmental performance of flames in the SCW medium should be attempted in the simplest possible experimental system. This system is meant to provide baseline data to be compared to results from similar experiments after the addition of a selected organic material to the SCW–methanol mixture. One of the main concerns that stands out in this evaluation is effect of flame oxidation processes on possible nitrogen oxides (NO_x) production due to high flame temperatures. This investigation presents new data on selected reaction products of air–methanol flames in a SCW

semi-batch system. Images of SCW flames are presented for the first time using Near Infrared (NIR) imaging, which is also used to propose a spontaneous ignition mechanism in the VFC.

2. Experimental

The main components of the visual flame cell and the experimental system used in our investigations are shown in Fig. 1. The main parts of the VFC are an air injection nozzle (1.2 mm i.d.) and the sapphire window section, in addition to an external heater surrounding the reaction cell (not shown). The cell has a total reaction volume of 15 ml and maximum operating conditions of 600 °C and 47 MPa. The air nozzle enters the system from the bottom and is positioned along the centerline of the reaction cell. The sapphire (4 mm thick, 10 mm free diameter) window port provides direct visual and optical access to the interior of the reaction cell, including the tip of the air nozzle where the flame is expected to ignite.

Water feed containing the desired fraction of methanol is drawn at room temperature by the HP liquid pump and loaded into the reaction cell. Once the desired pressure of 23 MPa is reached inside the reaction cell, the now-pressurized test solution is heated up to 400 °C. Meanwhile, ultra-dry air from industrial gas cylinders is drawn by the HP gas pump and loaded into the air reservoir at room temperature. As with the test solution, air is heated up to 400 °C inside the

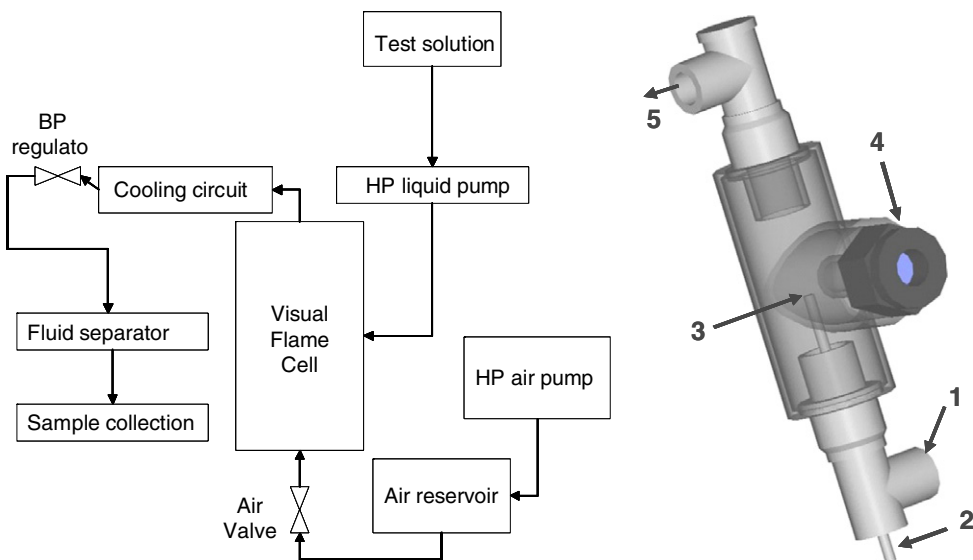


Fig. 1. To the left, schematic of experimental system components. To the right, visual flame cell (VFC) components shown are (1) test fluid loading port from HP liquid pump (2) air injection nozzle (3) tip of air nozzle where oxidation processes take place and flames form (4) sapphire window port (5) reaction products exit to cooling circuit, fluid separator, and sample collection.

reservoir once its desired pressure (30 MPa) is reached. The hot pressurized air is then kept in the reservoir at these conditions until the high-pressure test mixture in the reaction cell reaches supercritical temperatures (above 374 °C) required to ensure the homogeneity and/or dissolution of possible waste organic materials and for the spontaneous ignition of methanol. A back-pressure regulator maintains the reaction cell pressure below 27 MPa by releasing fluids upon pressure buildup in the system. When the test mixture is stable within the supercritical region, the air valve is opened and the heated air stream is allowed to flow into the supercritical mixture. If reaction parameters are adequate, a flame ignites spontaneously at the tip of the nozzle and could be observed, analyzed, and recorded through the sapphire window.

Once the oxidation reaction is complete and no flames or oxidation could be detected visually or thermally, the system is allowed to cool down and depressurize. Gas and liquid reaction products are then collected through the back-pressure regulator into the fluid separator for further sampling and analysis. Direct observations and analysis of SCW flames were recorded using CCD and Near Infrared (NIR) cameras. Two different Nova gas analyzers were used for all gaseous reaction products (CO , CO_2 , O_2 , and NO_x).

3. Results and discussion

Separate experimental runs were carried out at various combinations of operational conditions (fuel mixture and air temperatures, air flow-rate, and organic loading) to determine instantaneous flame ignition requirements in the VFC. Methanol proportions between 15 and 40 (v/v%) in water

were used as test fuel mixtures. Flame generation was attempted at fuel mixture temperatures between 250 and 400 °C. Air temperature also varied between 250 and 400 °C. In addition, different air flow-rates between 0.5 and 1.5 ml/min were examined. All experimental runs were carried out at system pressure of 23 MPa and air reservoir pressure of 30 MPa. Sub and super-critical ignition was achieved at a range of fuel proportions. However, only results from supercritical ignition are discussed in detail in this work.

3.1. Flame ignition and description

3.1.1. Ignition scenario

Flames were generally observed to ignite spontaneously up to 10–15 s after the injection of the preheated air stream into the fuel mixture. The videos of the VFC interior captured using the NIR camera (Fig. 3) were vital for explaining the considerable ignition delay. Figure 2 shows a proposed illustration of the conditions captured by the NIR camera through the sapphire view port. An illustration is preferred as actual images captured from the video were not clear enough to be presented in print, and also as it incorporates information from visual observations and temperature measurements within the reaction volume.

Upon injection of the air stream into the reaction volume, a thermocouple placed about 4 mm above the nozzle shows a drop in system temperature between 50 and 100 °C. Similarly, videos captured by the NIR camera detected the air stream as a lower temperature flux exiting the nozzle upon the introduction of the air into the supercritical mixture. NIR videos then show a higher temperature region developing near the walls of the reaction cell, which are in direct contact with the external heaters. Within a few seconds it could

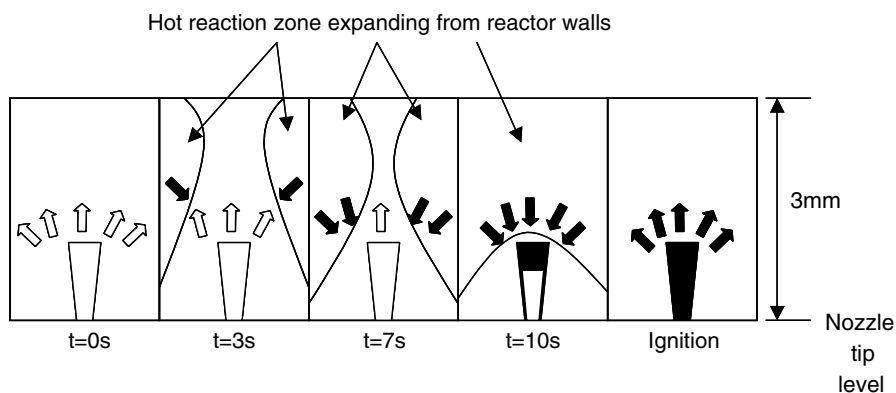


Fig. 2. For a reservoir air temperature of 390 °C and system temperature of 425 °C, thermocouples and NIR imaging reveal that air actually enters the system at about 300 °C. This low temperature plume (white arrows) reaches the hot walls and returns within 10 s (dark arrows) as a hot reaction zone to provide the air stream with enough energy to ignite spontaneously.

be observed that the hot region is expanding from the walls towards the center of reaction volume where it is resisted by the lower temperature air flux through the nozzle. Eventually, the hot plume does reach the tip of the nozzle and ignition of the methanol–air flame could clearly be seen to commence in the hot region down towards the nozzle tip (Fig. 2). Once the flame is ignited, it commences to burn upwards and registers temperatures several hundred degrees higher on the thermocouples with a corresponding change in NIR images where the flame becomes the hottest detected region.

Similar results were observed at all reservoir temperatures of the air (250–400 °C). It was observed, however, that an increase of reservoir temperature of air by 50 °C reduces ignition delay by 1–2 s. This indicates that no matter what the initial temperature of the high-pressure air prior to injection into the supercritical system, once the air valve is opened, significant heat loss occurs as the air stream begins to travel up the nozzle. This case of incoming air having a lower temperature could not be avoided even when the air reservoir temperatures were the maximum allowable temperatures for air valve operation. It could be concluded that the lower temperature air stream enters the system and travels to the hot wall regions, which are in direct contact with the external system heaters. The air stream reaches the hot walls and a higher temperature oxidation front is developed, which is countered by the lower temperature stream exiting the nozzle at the center of the reaction

volume. Eventually, after enough air enters the system for the hot reaction front to expand and come sufficiently close to the condensed air stream, ignition of the air stream occurs. Images captured from the NIR camera, and shown in Fig. 3, show the initial seconds after flame ignition and eventual stabilization, by lowering the air flow-rate from 1.5 to 0.5 ml/min, into a laminar conical inverse diffusion flame.

Based on the ignition mechanism proposed above, it would appear that the combustion processes in the VFC experimental system tend to be limited by physical mixing rather than chemical kinetics. Comparisons to existing literature on methanol–air flame kinetics were found to require complex adjustments to account for the complexities of the SCW flame system. In the comprehensive model developed by Dryer and Westbrook [8], flame inhibition at higher pressures was found to be due to dominance of certain chemical reactions over others as opposed to physical mixing limitations. Our system presents the added inhibition factor of the flame being generated in a water environment. On the other hand, it is proposed [8] that the higher the temperature of the unburnt gas region ahead of the flame the higher the fuel consumption and flame propagation rates. In our case, the high supercritical temperatures of the unburnt gas zone and the highly reactive SCW homogenous phase seem to overturn the inhibitive effect of the extremely high pressure in the system. Thus favoring the presence of higher concentrations of free radicals [8], which diffuse out of the flame front causing rapid fuel consumption and

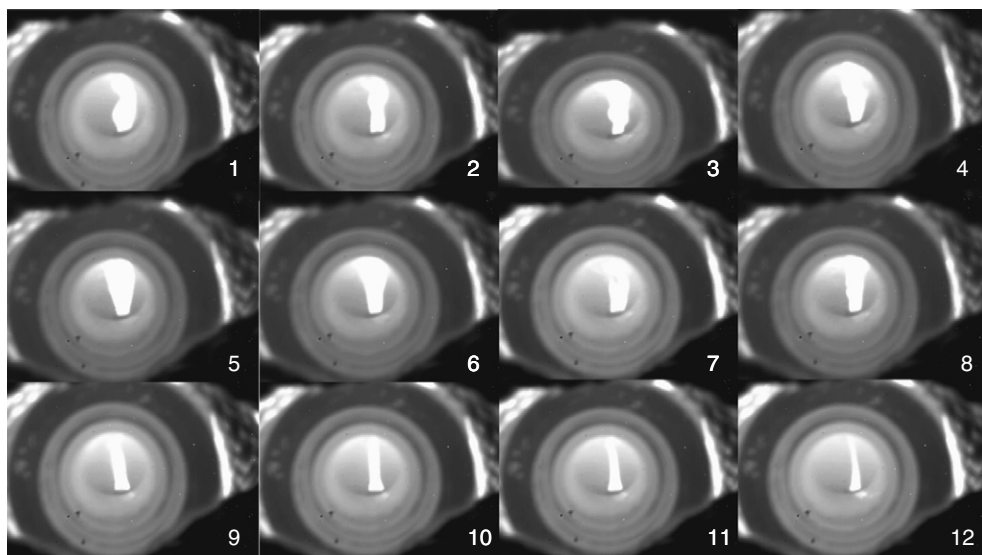


Fig. 3. Snapshots 1–12 showing an SCW air–methanol flame being stabilized by reducing air-flow from 1.5 to 0.5 ml/min. Picture sequence captured using a FLIR thermal imaging NIR camera. Reaction conditions: 23% methanol, SCW–methanol at 380 °C/23 MPa, air at 350 °C/30 MPa.

higher reaction rates, once the mixing limiting factor is overcome.

3.1.2. Flame description

It was observed that air stream temperatures below 290 °C did not induce spontaneous ignition of the methanol–air flame at any level of organic loading, although flameless oxidation could still be observed. No flame was generated at air flow-rates below 0.5 ml/min, while flame boundaries were unstable and experienced flickering and rapid extinction at air flow-rates above 1.5 ml/min. Flames could also be ignited at subcritical fuel mixture temperatures as low as 350 °C. Below this temperature of the water–methanol fuel mixture, no flame was observed even at air reservoir temperatures up to 400 °C and in those runs flameless oxidation was observed to be less efficient and the proposed ignition mechanism was not detected.

The most stable spontaneous flames were ignited at methanol volume fractions between 20 and 35% (v/v) methanol. In that fuel range, subcritical ignition was also achieved. This range was defined as the optimal flammability range inside the VFC. Flames generated in this range lasted between 5 and 10 s (Table 1) and caused significant increases in overall test fluid temperatures during those short durations. The various flame luminosities and colors were observed and compared visually. Flame luminosity was observed to be strongest at 23% methanol. This strong luminosity corresponded to a high recorded system temperature and highest NO_x production levels due to longest flame duration (10 s). Extinction of flames after the observed durations was due to depletion of the fuel in the reaction cell. This was verified as the flames re-ignited once a fresh volume of fuel was pumped into the reaction cell. No ignition was observed at methanol fractions below the optimal flammability limit (<20%). On the other hand, methanol fractions above 35% still showed unstable highly luminous short flame pulses which induced high almost instantaneous peak readings on system thermocouples (close to 1300 °C) and caused noticeable increases in overall system temperature despite their short durations. The generated flames are positioned directly along the air

nozzle axis and no flame elevation was observed. In some experimental runs ignition commenced abruptly and flames initially took turbulent vigorous forms. With control of the air flow-rate through the injection nozzle by adjusting the air valve, flames stabilized and assumed a near conical shape characteristic of diffusion flames. The height of the flame was observed to be most sensitive to changes in air flow-rate as opposed to changes in air stream temperature and methanol fraction in the system. A maximum flame height of 8–9 mm corresponded to 1.5 ml/min of 350 °C air stream.

3.2. Environmental performance

In all experimental runs in which the water–methanol reaction mixture reached near-supercritical conditions (21 MPa, 350 °C minimum) prior to air stream injection, little or no liquid product was generated after oxidation by air regardless of whether oxidation was in flame or flameless mode. Large volumes of flue gas were generated by the oxidation processes: oxidation of the 15 ml water–methanol test mixture in the flame cell reaction volume produced well over 5 L of flue gas after cooling and depressurization and prior to sample collection. It is clear from the proposed ignition mechanism (Fig. 2) that the gas samples collected would be a mix of the products of the flameless hot reaction zone that develops near the reaction cell walls and the eventual products due to delayed flame ignition. The mix of flame and flameless products did not need to be compared to flameless baseline regime and was not a major source of concern as these experimental runs are themselves intended to be baseline runs for future additions of more complex organics (such as naphthalene or decachlorobiphenyl) to the water–methanol mixture in order to fulfill the primary objective of this system by testing it as a potential environmental remediation tool.

Flue gas analysis revealed that 23% volume fraction of methanol in water is the optimal organic load for our experimental system. At this specific methanol fraction, maximum oxygen consumption, and CO₂ production rates were observed (Fig. 4). It is therefore expected, and

Table 1
Properties at different methanol proportions

Methanol (%)	Max temperature (°C)	System temperature (°C)	Duration (s)	Color	Luminosity
17	420	400	No flame	No flame	No flame
23	970	595	10	Green/blue	High
25	980	570	5	Light blue	Medium
29	960	565	6	Light orange	Medium
33	1010	590	8	Reddish orange	Low
44	(1292) pulses	515	0.5	White	High

Selected data points are methanol fractions where results demonstrate a change.

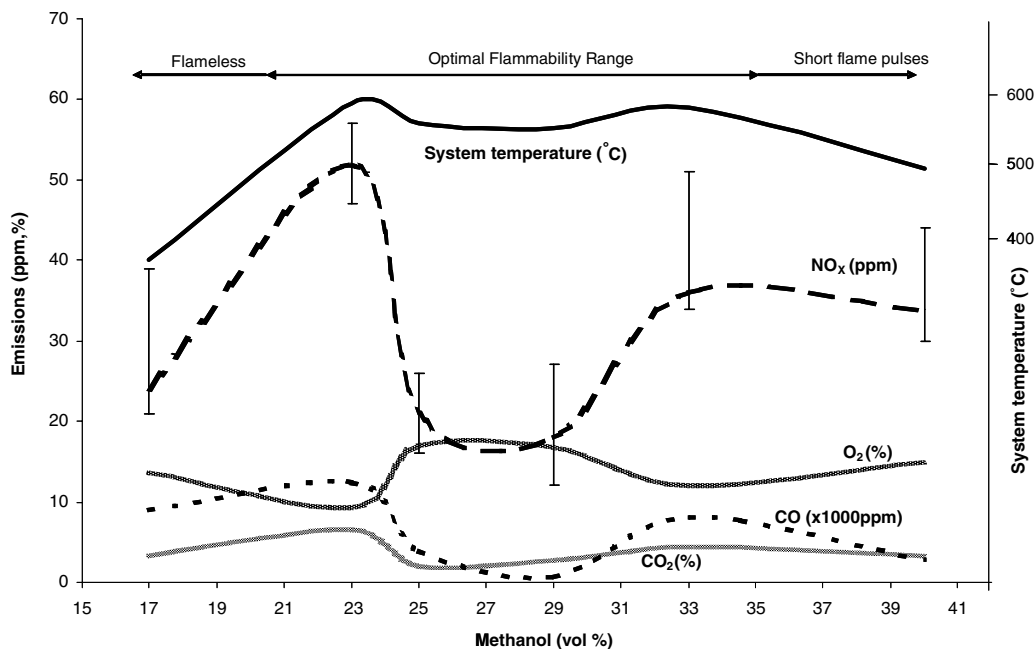


Fig. 4. Flue gas composition trends and system temperature changes at varying methanol proportions. The optimal flammability range in the VFC (20–35% methanol) is shown. No ignition occurred below this range, and only very short- and high-temperature ignition pulses occurred beyond it. Error bars shown for NO_x only. Other profiles shown have maximum errors of $\pm 15\%$.

was confirmed, that the highest flame temperature would occur at this methanol fraction. Results and carbon balances also showed that the presence of flames, compared to flameless oxidation, enhances oxidation of inlet organic carbon to CO_2 by an average 50% per additional unit methanol by volume. Higher reaction temperatures in flame oxidation regimes could explain this increase in oxidation efficiency. By examining raw data from system temperature profiles against flue gas compositions it could be observed that temperature of the system is the controlling factor in determining the efficiency of the combustion process. CO_2 , CO , NO_x , and O_2 followed system temperature profiles closely (Fig. 4). Consequently, CO_2 production and O_2 consumption are more efficient in flame oxidation mode within the optimal flammability range (20–35 (v/v%) methanol) when compared to flameless oxidation processes both within and outside the flammability range.

3.2.1. CO levels

In all runs, high levels of CO were observed. Concentrations between 800 and 12,000 ppm were measured in separate experimental runs (see Fig. 4). Carbon monoxide production in the system was always proportional to CO_2 production. It would have been expected that improved combustion conditions, such as improved air/fuel ratio and higher reaction temperature, would cause CO and CO_2 production trends to diverge by favoring

CO_2 production. It was found that this was not the case, and that the production trends remained similar at different system conditions. It was concluded that due to the batch nature of the reaction system and the low flow injection of air into the supercritical fuel mixture, oxygen “starvation” occurs in the reaction zone at the tip of the air nozzle. This starvation is a system characteristic present at all conditions and would inevitably lead to considerable CO production levels.

However, the most probable cause of the significantly high CO production levels is the relatively low temperature of the oxidizing air stream as well as the ignition mechanism (see Fig. 2). It could be assumed that the persistence of the low temperature air plume exiting the nozzle for several seconds would primarily be responsible for low temperature oxidation where significant levels of CO would be generated until ignited by the hot reaction zone originating from the walls of the VFC. Serikawa [6] reaches a similar conclusion attributing high CO production levels to low reaction temperatures rather than low oxygen levels.

3.2.2. NO_x levels

Flue gas analysis shows that, in our runs, NO_x production occurred even under flameless oxidation conditions in the hydrothermal system (Fig. 4). Temperature profiles (summary in Table 1) show that at methanol fractions above 35%, the

extremely short durations of flame pulses (0.5 s) are compensated by the higher temperatures of these pulses to cause an equally high average temperature as the longer duration stable flames. Figure 4 also shows the trends of NO_x formation with changes in system temperature. A minimum NO_x concentration of 18 ppm was produced in all runs. The maximum observed NO_x concentration was 52 ppm and it occurred at 23% methanol. This is the methanol fraction where the most efficient combustion occurred, most luminous flames were ignited, and high peak (970 °C) and system (595 °C) temperatures recorded (Table 1). The most likely explanation for appearance of NO_x even in lower temperature flameless runs is dominance of prompt NO_x formation kinetics in the system. Prompt NO_x production in combustion processes occurs at relatively low reaction temperatures and require the presence of C–H functional groups as intermediates for oxidation of nitrogen into nitrous oxide. This requirement is satisfied in our experimental runs by presence of organic loading in the fuel. Extremely rapid oxidation rates, short residence times, and enhanced reaction efficiencies in supercritical water media seem to support elevated prompt NO_x formation for both flame and flameless oxidation runs. The batch setup of the experimental system and the oxygen “starvation” condition discussed above could have caused the presence of a local fuel-rich zone at the tip of the air nozzle where oxidation reactions occur. The combination of these conditions contributes to prompt NO_x formation. By examining Fig. 4, it could be observed that minimal NO_x formation occurs between 25 and 30% methanol fractions. This range defines the conditions, above high-temperature combustion and below fuel-rich oxidation, where NO_x formation is minimized.

It has to be noted that within the extremely limited literature on flames in supercritical water, only a single research paper [6] published results where air was used as the oxidizing agent as opposed to pure oxygen. That meant that NO_x production would only be a major concern for Serikawa as a considerable nitrogen volume is introduced within the air stream into the supercritical system. However, Serikawa states that “(n)either NO_2 (n)or NO was detected during all SCWO run(s)” [6, p. 1153], and presents no data whatsoever on NO_x production, even in runs where flames were generated and sustained for several minutes. Therefore, ours could be considered the first paper to report and analyze NO_x formation in SCW flame regimes.

4. Conclusions

A visual flame cell (VFC) was designed for generation, description, and environmental eval-

uation of high-pressure SCW flames as a step in evaluating feasibility of their use as an environmental remediation tool for destruction of complex organic wastes in a practical application. The system was operated in a semi-batch mode and flames were successfully ignited spontaneously at different proportions of methanol as an organic fuel and air as an oxidizing agent. An optimal flammability range of 20–35 (v/v%) methanol was determined for the experimental system. NIR flame imaging revealed, in conjunction with temperature measurement and visual imaging, a combustion mechanism specific to the VFC design that retards ignition and promotes CO production. Flue gas analysis revealed that optimal combustion conditions occur at 23% methanol fraction and are accompanied by high luminosity flames as well as high CO and NO_x production. CO generation was found to be high in all experimental runs. NO_x formation trends were directly related to the system temperature where they were produced at low reaction temperatures and flameless oxidation modes. The optimal range for minimization of NO_x production was 25–30 (v/v%) methanol. It was proposed that operation in the batch mode and low flow air stream injection caused a fuel-rich oxygen-starved zone at the tip of the air injection nozzle. Thus, in conjunction with the proposed ignition mechanism, it explains enhanced CO production in low oxygen conditions, and favors prompt NO_x formation due to abundance of C–H bonds and efficient reaction conditions in supercritical water. It was found that if organic loading was lowered sufficiently to minimize CO and eliminate prompt NO_x formation, high oxidation efficiencies were still achieved but no flames were generated.

Acknowledgments

We wish to acknowledge the financial support from the Natural Sciences and Engineering Research Council of Canada through Discovery, Strategic and Equipment grants (NSERC Grants OGP-170464, STP-269866, and EQ-PEQ-252297). We also thank Drs. Mirela Barsan, Fadi el Dabbagh, Zhen Fang, and Mr. Sherif Barakat for their input; Mr. Andrew Tohn for his excellent experimental skills, and Mr. Tomasz Nowak for outstanding graphics support.

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Comments

Sébastien Candel, EM2C; CNRS; Ecole Centrale Paris, France. In your initial system, where you burn methanol in supercritical water, a diffusion flame is being formed and as it evolves in time a layer of products accumulates around the flame. The fuel diffusion flux is progressively diminished possibly leading to extinction before total oxidation of the methanol introduced in the cell.

Reply. The stage when methanol is burned is not the initial system. In fact, the system is exposed to the transition from ambient to supercritical water conditions for a considerable duration prior to introduction of air for ignition. Depending on the heating rate of the system, methanol could be partially consumed by hydrolysis prior to ignition.

Based on the 15 ml reaction volume, TOC analysis shows methanol conversion level generally well above 90%. However, other components of the experimental system, which is run in a semi-batch mode, do indeed contain an additional supply of methanol which stays un-reacted within the system due to its distance from the heated reaction volume. Therefore, accumulation of combustion products may indeed lead to extinction of the flame prior to consumption of additional methanol in the adjacent lower-temperature system components (methanol–water feed tube, cooling circuit). These components are located outside the reaction volume (Fig. 1). This condition might be adjustable by running the system in a full continuous mode. The question of a continuous sys-

tem is addressed below in the reply to the second comment on this paper.

●

Ken Brezinsky, University of Illinois, Chicago, USA. Even though your flame experiment looks like a flow system it is actually a closed system. Does that not lead to all the problems with ignition delay? Could you eliminate this problem by developing a flow system?

Reply. The system is operated in a semi-batch mode. A flow is established through the system only upon pressure loss below supercritical levels. However, during ignition, the system is effectively a closed batch system. Attributing the ignition delay solely to the closed nature of the system is not necessarily valid, as instantaneous ignition was indeed observed when the pre-heat temperature of the air was sufficiently high (above 475 °C). However, this condition could not be readily repeated as it required the air control valve to operate above the safe level.

In terms of possibly eliminating the ignition delay by running the system in the continuous mode, the same limitation would still apply as the pre-heat temperature of the air would not be sufficiently high for an instantaneous ignition. In addition, bringing all system reactants (methanol/water, air) to supercritical temperature and pressure in a continuous mode would be virtually impossible without major changes to the current simple design and common system materials.